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Hyperfine energy levels of alkali-metal dimers: Ground-state homonuclear molecules in magnetic fields

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We investigate the hyperfine energy levels and Zeeman splittings for homonuclear alkali-metal dimers in low-lying rotational and vibrational states, which are important for experiments designed to produce quantum gases of deeply bound molecules. We carry out density-functional theory calculations of the nuclear hyperfine coupling constants. For nonrotating states, the zero-field splittings are determined almost entirely by the scalar nuclear spin-spin coupling constant. By contrast with the heteronuclear case, the total nuclear spin remains a good quantum number in a magnetic field. We also investigate levels with rotational quantum number $N=1$, which have long-range anisotropic quadrupole-quadrupole interactions and may be collisionally stable. For these states the splitting is dominated by nuclear quadrupole coupling for most of the alkali-metal dimers and the Zeeman splittings are considerably more complicated.

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I. INTRODUCTION

There have been enormous advances over the last year in experimental methods to produce ultracold molecules in their rovibrational ground state at microkelvin temperatures. Ospelkaus *et al.* [1] produced KRb molecules in high-lying states by magnetoassociation (Feshbach resonance tuning) and then transferred them by stimulated Raman adiabatic passage to levels of the $^1\Sigma^+$ ground state bound by more than 10 GHz. This was then extended by Ni *et al.* [2] to produce molecules in $(v, N)=(0, 0)$, where v and N are the quantum numbers for molecular vibration and mechanical rotation. Danzl *et al.* [3,4] have carried out analogous experiments on Cs dimers, while Lang *et al.* [5,6] have produced Rb₂ molecules in the lowest rovibrational level of the lowest triplet state. There have also been considerable successes in direct photoassociation to produce low-lying states [7–10].

A major goal of the experimental work is to produce a stable molecular quantum gas. However, such a gas can form only if (i) a large number of molecules are in the same hyperfine state and (ii) the molecules are stable to collisions that occur in the gas. In particular, inelastic collisions that transfer internal energy into relative translational energy cause heating and/or trap loss. It is thus very important to understand the hyperfine structure of the low-lying levels and its dependence on applied electric and magnetic fields. In a previous paper, we explored the hyperfine levels of heteronuclear alkali-metal dimers in rotationless levels [11]. The purpose of the present paper is to extend this work to homonuclear molecules, which have important special features. We also explore $N=1$ levels, which may be collisionally stable for homonuclear molecules and which interact with longer-range forces than $N=0$ levels.

II. MOLECULAR HAMILTONIAN

The Hamiltonian of a diatomic molecule in the presence of an external magnetic field can be decomposed into five

different contributions: the electronic, vibrational, rotational, hyperfine, and Zeeman terms. For $^1\Sigma$ molecules in a fixed vibrational level, the first two terms take a constant value and the rotational, hyperfine, and Zeeman parts of the Hamiltonian may be written [12–14]

$$H = H_{\text{rot}} + H_{\text{hf}} + H_Z, \quad (1)$$

where

$$H_{\text{rot}} = B_v N^2 - D_v N^2 \cdot N^2, \quad (2)$$

$$\begin{aligned} H_{\text{hf}} &= H_Q + H_{\text{IN}} + H_t + H_{\text{sc}} \\ &= \sum_{i=1}^2 V_i : Q_i + \sum_{i=1}^2 c_i N \cdot I_i + c_3 I_1 \cdot T \cdot I_2 \\ &\quad + c_4 I_1 \cdot I_2, \end{aligned} \quad (3)$$

$$H_Z = -g_t \mu_N N \cdot B - \sum_{i=1}^2 g_i \mu_N I_i \cdot B (1 - \sigma_i), \quad (4)$$

where the index i refers to each of the nuclei in the molecule. N , I_1 , and I_2 represent the operators for mechanical rotation and for the spins of nuclei 1 and 2. The rotational and centrifugal constants of the molecule are given by B_v and D_v (but centrifugal distortion is neglected in the present work). We use N rather than J for mechanical rotation because we wish to reserve J for the angular momentum including electron spin for future work on triplet states.

The hyperfine Hamiltonian of Eq. (3) consists of four different contributions. The first is the electric quadrupole interaction H_Q , with coupling constants $(eqQ)_1$ and $(eqQ)_2$. It represents the interaction of the nuclear quadrupoles (eQ_i) with the electric field gradients q_i created by the electrons at the nuclear positions. The second is the spin-rotation term H_{IN} , which describes the interaction of the nuclear magnetic moments with the magnetic moment created by the rotation of the molecule. Its coupling constants are c_1 and c_2 . For a homonuclear molecule with identical nuclei, $(eqQ)_1 = (eqQ)_2$ and $c_1 = c_2$. The last two terms represent the interaction between the two nuclear spins; there is both a tensor

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TABLE I. Nuclear quadrupole moment (Q), electric quadrupole coupling constant (eqQ), nuclear g factor (g), spin-rotation coupling constant (c_1), tensor spin-spin coupling constant (c_3), scalar spin-spin coupling constant (c_4), absolute value of the $c_4/(eqQ)$ ratio, isotropic part of the nuclear shielding (σ) and rotational g factor (g_r) for the homonuclear alkali dimers. All the quantities except the nuclear quadrupole moments, the nuclear g factors and the rotational g factors were evaluated using DFT calculations (see Sec. III). Both experimental [17] and theoretical results are presented for Na_2 .

	Q (fm ²)	eqQ (MHz)	g	c_1 (Hz)	c_3 (Hz)	c_4 (Hz)	$ c_4/(eqQ) $	σ (ppm)	g_r
$^6\text{Li}_2$	-0.082	0.00123	0.822	161	137	32	0.026	102	0.1259
$^7\text{Li}_2$	-4.06	0.0608	2.171	365	955	226	0.0037	102	0.1080
$^{23}\text{Na}_2$ (expt.)	10.45	-0.459	1.479	243	303	1067	0.0023		0.0386
$^{23}\text{Na}_2$ (DFT)		-0.456		299	298	1358	0.0030	613	
$^{39}\text{K}_2$	5.85	-0.290	0.261	35	5	106	0.00036	1313	0.0212
$^{40}\text{K}_2$	-7.3	0.362	-0.324	-42	8	163	0.00045	1313	0.0207
$^{41}\text{K}_2$	7.11	-0.353	0.143	18	2	32	0.000091	1313	0.0202
$^{85}\text{Rb}_2$	27.7	-2.457	0.541	63	30	2177	0.00089	3489	0.0095
$^{87}\text{Rb}_2$	13.4	-1.188	1.834	209	346	25021	0.021	3489	0.0093
$^{133}\text{Cs}_2$	-0.355	0.0486	0.738	96	119	12993	0.27	6461	0.0054

component H_t , with coupling constant c_3 , and a scalar component H_{sc} , with coupling constant c_4 . The second-rank tensor T represents the angular part of a dipole-dipole interaction.

The Zeeman Hamiltonian H_Z has both rotational and nuclear Zeeman contributions characterized by g factors g_r , g_1 , and g_2 . For homonuclear molecules $g_1=g_2$. The nuclear shielding tensor σ_i is approximated here by its isotropic part σ_i ; terms involving the anisotropy of σ_i are extremely small for the states considered here.

The nuclear g factors and the quadrupole moments of the nuclei are experimentally known [15]. For homonuclear molecules we neglect the effect of electric fields, though in principle there are small effects due to anisotropic polarizabilities and the molecular quadrupole moments can interact with the gradients of inhomogeneous fields.

III. EVALUATION OF THE COUPLING CONSTANTS

The rotational g factors are known experimentally for all the homonuclear alkali-metal dimers [16]. However, the only such species for which the nuclear hyperfine coupling constants have been determined accurately is Na_2 [17]. We have therefore evaluated the remaining coupling constants using density-functional theory (DFT) calculations performed with the Amsterdam density functional (ADF) package [18,19] with all-electron basis sets and including relativistic corrections. A full description of the basis sets, functionals, etc. used in the calculations has been given in our previous paper on heteronuclear systems [11]. In the present work, the calculations were carried out at the equilibrium geometries ($R_e=2.67$ Å for Li_2 [20], 3.08 Å for Na_2 [21], 3.92 Å for K_2 [22], 4.21 Å for Rb_2 [23], and 4.65 Å for Cs_2 [24]). This gives results that are approximately valid not only for $v=0$ states but also for other low-lying vibrational states.

The values for the coupling constants are given in Table I. It may be seen that the DFT results for Na_2 are within about 30% of the experimental values, and similar accuracy was

obtained for other test cases in our previous work [11]. The accuracy is likely to be comparable for the other cases studied here. This level of accuracy is adequate for the purpose of the present paper, which aims to explore the qualitative nature of the Zeeman patterns. Most of our conclusions are insensitive to the exact magnitudes of the coupling constants.

IV. HYPERFINE ENERGY LEVELS

Our previous work [11] showed that the zero-field splitting for heteronuclear diatomic molecules in $N=0$ states is determined almost entirely by the scalar nuclear spin-spin interaction. This remains true for homonuclear molecules in $N=0$ states. We show below that for $N>0$ the electric quadrupole interaction is dominant for all the homonuclear dimers except Cs_2 and $^6\text{Li}_2$, with smaller but significant contributions from the remaining coupling constants.

For all systems except Li_2 , the scalar spin-spin coupling is considerably stronger than the spin-rotation and tensor spin-spin couplings. Knowledge of the nuclear quadrupole coupling constant eqQ and the scalar spin-spin coupling constant c_4 is therefore sufficient to understand the hyperfine splitting patterns. We will focus here on $^{85}\text{Rb}_2$ and $^{87}\text{Rb}_2$, which form a convenient pair that approximately cover the range of values of the ratio $|c_4/(eqQ)|$. Lang *et al.* [6] have produced $^{87}\text{Rb}_2$ in the lowest rovibrational level of the lowest triplet state, but as far as we are aware not yet in the singlet state.

The hyperfine energy levels are obtained by diagonalizing the matrix representation of the Hamiltonian (1) in a basis set of angular momentum functions. In order to facilitate the assignment of quantum numbers to the energy levels, two different basis sets are employed,

$$|(I_1 I_1) I M_I N M_N\rangle \quad (\text{spin-coupled basis}), \quad (5)$$

$$|(I_1 I_1) I N F M_F\rangle \quad (\text{fully coupled basis}), \quad (6)$$

where I and F are the total nuclear spin and total angular momentum quantum numbers and M_I and M_F are their pro-

TABLE II. Values of I permitted by the nuclear exchange symmetry for even and odd rotational levels of $^{85}\text{Rb}_2$ and $^{87}\text{Rb}_2$ in $^1\Sigma_g^+$ states.

	N	I
$^{85}\text{Rb}_2(I_{\text{Rb}}=5/2)$	Even	0, 2, 4
	Odd	1, 3, 5
$^{87}\text{Rb}_2(I_{\text{Rb}}=3/2)$	Even	0, 2
	Odd	1, 3

jections onto the Z axis defined by the external field. The matrix elements of the different terms in the Hamiltonian in each of the basis sets are calculated through standard angular momentum techniques [25]. Explicit expressions are given in the Appendix.

For homonuclear molecules, nuclear exchange symmetry dictates that not all possible values of the total nuclear spin I can exist for each rotational level. For molecules in Σ_g^+ or Σ_u^- states, only even I values can exist for even N and only odd I for odd N . This is true for either fermionic or bosonic nuclei but is reversed for Σ_u^+ or Σ_g^- states. Table II summarizes the I - N pairs compatible with the antisymmetry of the wave function under nuclear exchange for the Rb₂ isotopomers.

A. Zeeman splitting for $N=0$ homonuclear alkali dimers

The Zeeman splittings for the $N=0$ hyperfine levels of $^{85}\text{Rb}_2$ and $^{87}\text{Rb}_2$ are shown in Fig. 1. The zero-field splittings are in most respects similar to those found for heteronuclear molecules in the ground rotational state [11]. The similarities can be summarized as follows.

(1) The scalar nuclear spin-spin interaction and the nuclear Zeeman effect are the only two terms in the molecular Hamiltonian with nonzero diagonal elements for $N=0$.

(2) The electric quadrupole and the tensor nuclear spin-spin interactions are not diagonal in N , coupling the N , $N+2$, and $N-2$ rotational levels. This means that the energy levels should be converged by including in the calculations as many rotational levels as necessary. However, the coupling constants eQq and c_3 are very much smaller than the rotational spacings, so that in practice it is adequate to include one excited rotational level. Convergence for $N=0$ is reached with $N_{\text{max}}=2$ and convergence for $N=1$ is reached with $N_{\text{max}}=3$.

(3) The scalar spin-spin interaction is diagonal in both the spin-coupled and fully coupled basis sets, which for $N=0$ are identical,

$$\begin{aligned} \langle (N=0)IM_I | c_4 \mathbf{I}_1 \cdot \mathbf{I}_2 | (N=0)IM_I \rangle \\ = \frac{1}{2} c_4 [I(I+1) - 2I_{\text{Rb}}(I_{\text{Rb}}+1)]. \end{aligned} \quad (7)$$

Except for a very small contribution coming from the coupling with $N=2$ levels, these diagonal elements determine the zero-field splitting.

Despite the similarity of the zero-field levels, there are important differences between the Zeeman splittings for het-

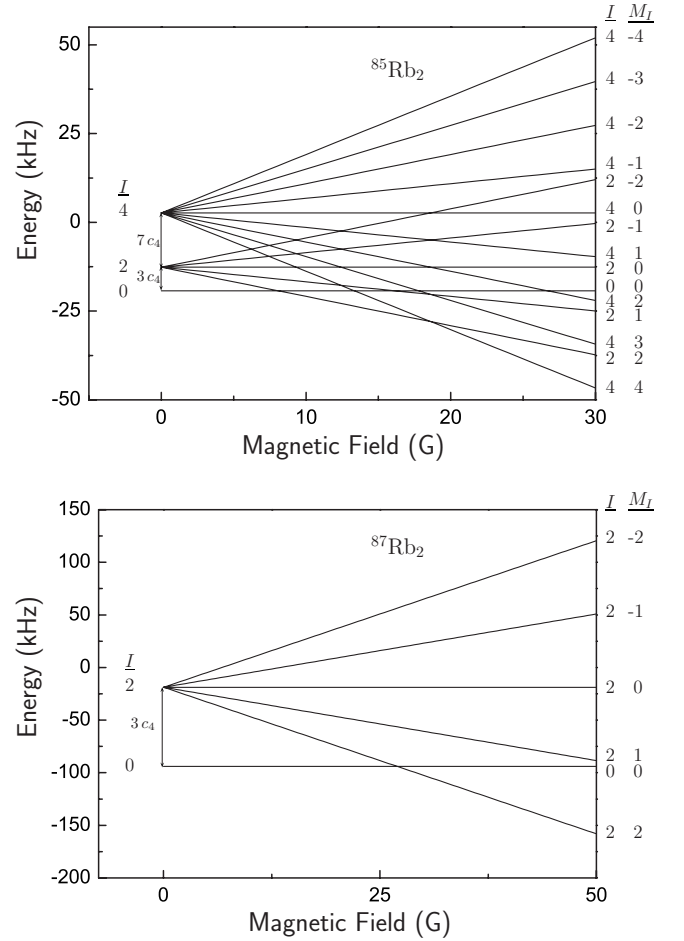


FIG. 1. Zeeman splitting of hyperfine levels for $N=0$ states of $^{85}\text{Rb}_2$ (upper panel) and $^{87}\text{Rb}_2$ (lower panel).

eronuclear and homonuclear molecules. For heteronuclear dimers [11], levels with the same M_I but different I exhibit avoided crossings as a function of magnetic field. Because of this, I is no longer a good quantum number at high field but the individual nuclear spin projections M_{I1} and M_{I2} become nearly conserved. For homonuclear dimers, however, different energy levels that correspond to the same value of M_I are parallel, so that no avoided crossings appear as a function of the field. Both I and M_I remain good quantum numbers regardless of the value of the magnetic field but M_{I1} and M_{I2} are not individually conserved. This is illustrated in Fig. 1. It arises because the nuclear Zeeman term, which is the only nondiagonal term for $N=0$ in the heteronuclear case, is diagonal for homonuclear molecules. Its nonzero elements are given by Eq. (A11) of the Appendix,

$$\langle (N=0)IM_I | H_{IZ} | (N=0)IM_I \rangle = -g_{\text{Rb}}\mu_N B_Z (1 - \sigma_{\text{Rb}}) M_I. \quad (8)$$

The nuclear Zeeman term is diagonal because the g factors of the two nuclei are equal and not because of nuclear exchange symmetry. The $N=0$ block of the molecular Hamiltonian for a heteronuclear dimer with two identical nuclear g factors would also be diagonal.

The conservation of the total nuclear spin I and nonconservation of M_{I1} and M_{I2} at high fields may have important consequences for the selection rules in spectroscopic transitions used to produce ultracold molecules and for the collisional stability of molecules in excited hyperfine states.

B. Zeeman splitting for $N=1$ homonuclear alkali dimers

Ultracold homonuclear molecules in $N=1$ states are particularly interesting because they are likely to be stable with respect to inelastic collisions to produce $N=0$, at least for collisions with nonmagnetic species such as other molecules in $^1\Sigma$ states. Such collisions cannot change the nuclear spin symmetry and thus cannot change N from odd to even. Inelastic collisions may well be stronger for collisions of molecules in triplet states because of magnetic interactions between electron and nuclear spins. Transitions between odd and even rotational levels are permitted in atom-exchange collisions, such as occur in collisions with alkali-metal atoms [26–31].

Homonuclear molecules do not possess electric dipole moments but do have quadrupole moments. The quadrupole-quadrupole interaction is anisotropic and is proportional to R^{-5} , so is longer range than the R^{-6} dispersion interaction that acts between neutral atoms and molecules. The quadrupole-quadrupole interaction averages to zero for rotationless states ($N=0$), but not for $N>0$. Quantum gases of rotating homonuclear molecules may thus exhibit anisotropic effects.

For $N>0$, all the terms in the Hamiltonian (1) have matrix elements diagonal in N . Some of these are nondiagonal in hyperfine quantum numbers, so the energy level patterns are much more intricate. The zero-field splitting is dominated in most cases by the electric quadrupole interaction and the scalar nuclear spin-spin term. The remaining constants (c_1 and c_3) make much smaller contributions except for the two Li_2 isotopomers. For $^6\text{Li}_2$, all the terms in the hyperfine Hamiltonian contribute significantly. For $^7\text{Li}_2$, the splitting is dominated by the electric quadrupole interaction but contributions from all the remaining terms are significant.

Figure 2 shows the “building-up” of the zero-field $N=1$ hyperfine energy levels for $^{85}\text{Rb}_2$ and $^{87}\text{Rb}_2$ in three steps: first, only the rotational and the electric quadrupole terms are considered; second, the scalar spin-spin interaction is included; and third, the spin-rotation and the tensor spin-spin interaction terms are added to complete the hyperfine Hamiltonian. For $^{85}\text{Rb}_2$, the electric quadrupole term alone determines the energy level pattern, while for $^{87}\text{Rb}_2$ there is a significant additional contribution from the scalar spin-spin interaction, attributable to the relatively large value of c_4 for this molecule (see Table I).

The quantum numbers that label the zero-field energy levels are included in Fig. 2. The total angular momentum quantum number F is always a good quantum number at zero field. In some cases, when there is only one pair of values I and N that can couple to give the resultant F , I is also a good quantum number. Otherwise, I is mixed and the values given in Fig. 2 are ordered according to their contribution to the

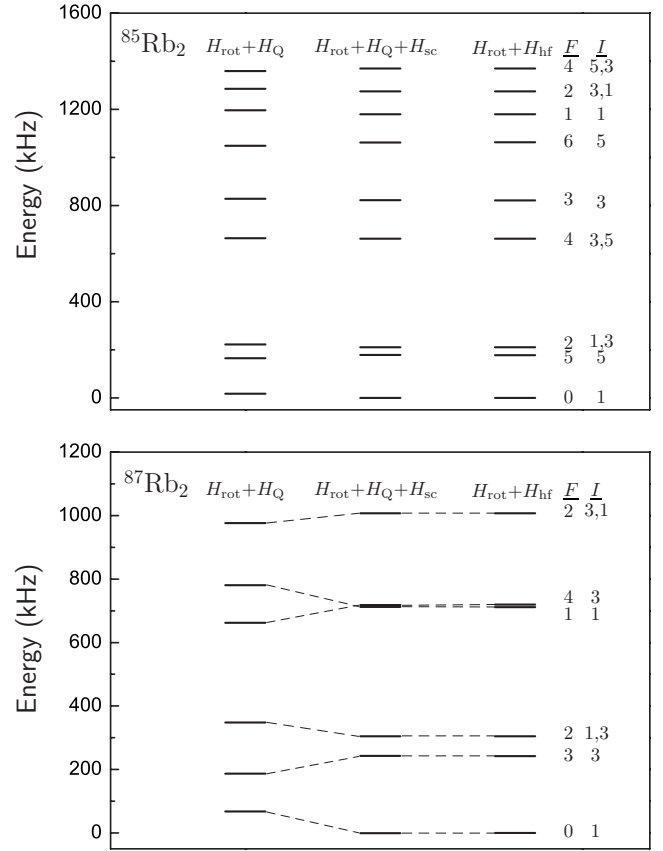


FIG. 2. Zero-field hyperfine splitting for $N=1$ states of $^{85}\text{Rb}_2$ (upper panel) and $^{87}\text{Rb}_2$ (lower panel). For each species, the hyperfine energy levels obtained when only the rotational and electric quadrupole terms are included are shown in the left column. The effect of adding the scalar spin-spin interaction is displayed in the central column and, finally, the right column shows the splitting when the whole hyperfine Hamiltonian is considered. All the energies are referred to the lowest hyperfine level for the complete Hamiltonian.

eigenstate: the first quantum number listed identifies the largest contribution.

The Zeeman splittings for $N=1$ states of $^{85}\text{Rb}_2$ and $^{87}\text{Rb}_2$ for different ranges of magnetic fields are shown in Figs. 3 and 4. Each zero-field level splits into $2F+1$ states with different projection quantum numbers M_F . Although in principle both the nuclear (H_{Iz}) and the rotational (H_{Nz}) Zeeman terms contribute to the splitting, $g_{\text{Rb}} \gg g_r$ so that the rotational Zeeman term contributes only about 1% for $^{85}\text{Rb}_2$ and less than 0.5% for $^{87}\text{Rb}_2$.

In contrast with the $N=0$ case, the Hamiltonian for $N=1$ is not diagonal and energy levels corresponding to the same M_F value display avoided crossings. The magnetic field values at which the avoided crossings are found, between 0 and 2000 G for $^{85}\text{Rb}_2$ (lower panel of Fig. 4) and between 0 and 200 G for $^{87}\text{Rb}_2$ (lower panel of Fig. 3), scale with the ratio between the electric quadrupole constant and the nuclear g factor.

For larger magnetic fields, M_I and M_N become individually good quantum numbers and the energy levels corresponding to the same value of M_I gather together. Both fea-

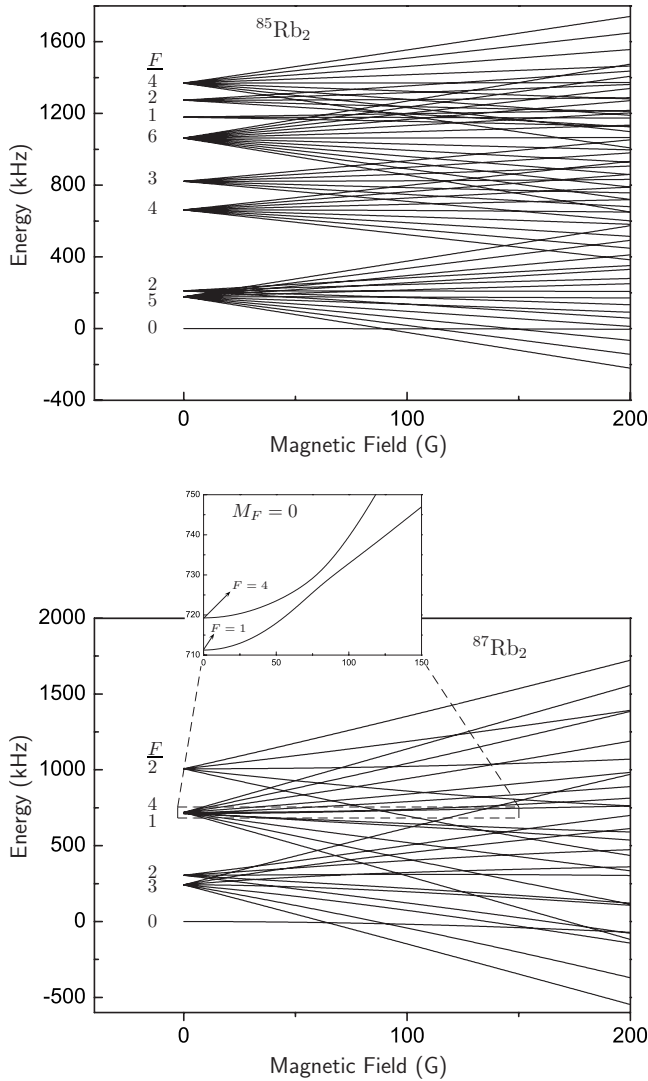


FIG. 3. Zeeman splitting for $N=1$ states of $^{85}\text{Rb}_2$ (upper panel) and $^{87}\text{Rb}_2$ (lower panel). The inset for $^{87}\text{Rb}_2$ shows the avoided crossing of $M_F=0$ states.

tures are illustrated in Fig. 4 where, for the sake of clarity, the values of M_N are included only in the lower panel. Equation (A11) shows that the matrix representation of the nuclear Zeeman term in the spin-coupled basis is diagonal with nonzero elements proportional to M_I and independent of any other quantum number. As the magnetic field increases the nuclear Zeeman terms become dominant and the slope of the energy levels is determined by M_I .

The results in Fig. 4 neglect the diamagnetic Zeeman interaction, which is not completely negligible at the highest fields considered (up to 4000 G). The justification for this is as follows. The Hamiltonian for the diamagnetic Zeeman interaction [12] consists of two terms proportional to the square of the magnetic field: one depends on the trace of the magnetizability tensor and the other is proportional to its anisotropic part. The first term has a value around 200 kHz at 4000 G for $^{85}\text{Rb}_2$. Although this quantity is not negligible, it has not been included because it simply shifts all the energy levels by the same amount and has no effect on splittings. The second term is diagonal in the spin-coupled basis set and

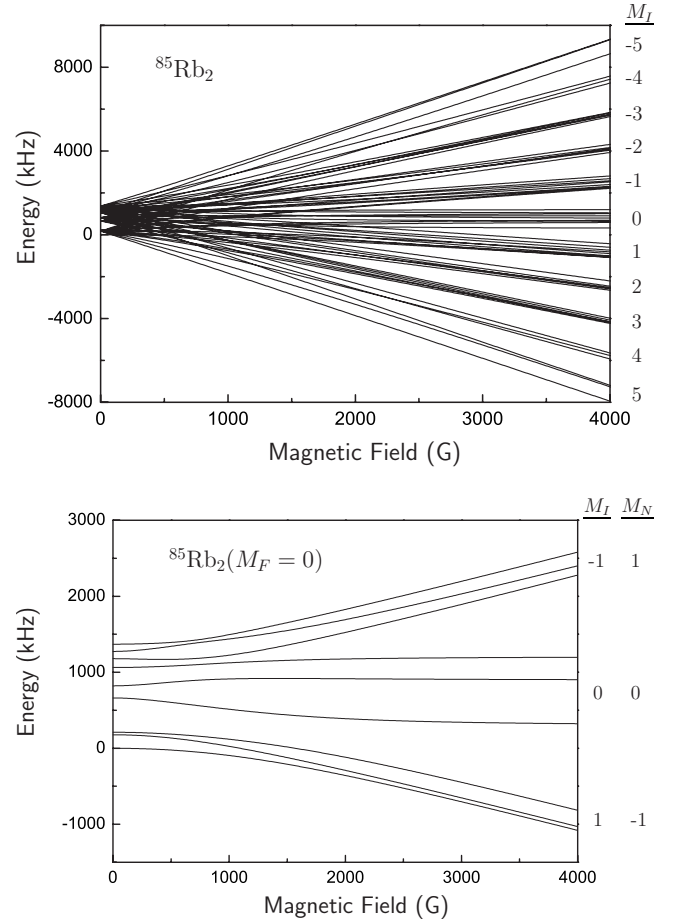


FIG. 4. Zeeman splitting for $N=1$ states of $^{85}\text{Rb}_2$. The avoided crossings for $M_F=0$ are shown in the lower panel.

its nonzero elements depend on N and M_N . For $^{85}\text{Rb}_2$ at 4000 G it would shift the energy levels by about 15 kHz. It is therefore very small compared to the nuclear Zeeman effect.

V. CONCLUSIONS

We have explored the hyperfine energy levels and Zeeman splitting patterns for low-lying rovibrational states of homonuclear alkali-metal dimers in $^1\Sigma$ states. We have calculated the nuclear hyperfine coupling constants for all common isotopic species of the homonuclear dimers from Li_2 to Cs_2 and explored the energy level patterns in detail for $^{85}\text{Rb}_2$ and $^{87}\text{Rb}_2$.

For rotationless molecules ($N=0$ states), the zero-field splitting arises almost entirely from the scalar nuclear spin-spin coupling. The levels are characterized by a total nuclear spin quantum number I and states with different values of I are separated by amounts between 90 Hz for $^{41}\text{K}_2$ and 160 kHz for $^{133}\text{Cs}_2$. When a magnetic field is applied, each level splits into $2I+1$ components but all the levels with a particular value of M_I are parallel. This is different from the heteronuclear case, and for homonuclear molecules I remains a good quantum number in a magnetic field. However, the projection quantum numbers M_{I1} and M_{I2} for individual nu-

clei do not become nearly good quantum numbers at high fields for homonuclear molecules. These differences in quantum numbers may have important consequences for spectroscopic selection rules and for the collisional stability of molecules in excited hyperfine states.

Molecules in excited rotational states are also of considerable interest. In particular, molecules in $N=1$ states may be collisionally stable because transitions between even and odd rotational levels require a change in nuclear exchange symmetry. Molecules in excited rotational states have anisotropic quadrupole-quadrupole interactions that are longer-range than dispersion interactions. The hyperfine energy level patterns are considerably more complicated for $N=1$ states than for $N=0$ states and I is not in general a good quantum number even at zero field.

The results of the present paper will be important in studies that produce ultracold molecules in low-lying rovibrational levels, where it is important to understand and control the population of molecules in different hyperfine states.

ACKNOWLEDGMENTS

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APPENDIX

Explicit expressions for the matrix elements of the molecular Hamiltonian terms are now provided in the spin-coupled and fully-coupled basis sets. The equations are valid for homonuclear molecules.

The matrix elements for the rotational term (H_{rot}) are given by

$$\begin{aligned} \langle NM_N(I_1 I_1) IM_I | H_{\text{rot}} | N' M_{N'}(I_1 I_1) I' M_{I'} \rangle \\ = \delta_{NN'} \delta_{M_N M_{N'}} \delta_{II'} \delta_{M_I M_{I'}} B N(N+1), \end{aligned} \quad (\text{A1})$$

$$\begin{aligned} \langle N(I_1 I_1) IFM_F | H_{\text{rot}} | N'(I_1 I_1) I' F' M_{F'} \rangle \\ = \delta_{NN'} \delta_{II'} \delta_{FF'} \delta_{M_F M_{F'}} B N(N+1). \end{aligned} \quad (\text{A2})$$

The matrix elements for the electric quadrupole interaction (H_Q) are given by

$$\begin{aligned} \langle NM_N(I_1 I_1) IM_I | H_Q | N' M_{N'}(I_1 I_1) I' M_{I'} \rangle \\ = \frac{(eqQ)_1}{4} (-1)^{2I_1} \{4(2N+1)(2N'+1)(2I+1)(2I'+1)\}^{1/2} \\ \times \begin{pmatrix} N & 2 & N' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} I_1 & 2 & I_1 \\ -I_1 & 0 & I_1 \end{pmatrix}^{-1} \begin{Bmatrix} I_1 & I & I_1 \\ I' & I_1 & 2 \end{Bmatrix} \\ \times \sum_{FM_F} \left[(-1)^{F+2M_F} (2F+1) \begin{pmatrix} N & I & F \\ M_N & M_I & -M_F \end{pmatrix} \right. \\ \left. \times \begin{pmatrix} N' & I' & F \\ M_{N'} & M_{I'} & -M_F \end{pmatrix} \begin{Bmatrix} I & N & F \\ N' & I' & 2 \end{Bmatrix} \right], \end{aligned} \quad (\text{A3})$$

$$\begin{aligned} \langle N(I_1 I_1) IFM_F | H_Q | N'(I_1 I_1) I' F' M_{F'} \rangle \\ = \delta_{FF'} \delta_{M_F M_{F'}} \frac{(eqQ)_1}{4} (-1)^{N+N'+F+2I_1} \{4(2N+1) \\ \times (2N'+1)\}^{1/2} \times \{(2I+1)(2I'+1)\}^{1/2} \begin{pmatrix} N & 2 & N' \\ 0 & 0 & 0 \end{pmatrix} \\ \times \begin{pmatrix} I_1 & 2 & I_1 \\ -I_1 & 0 & I_1 \end{pmatrix}^{-1} \begin{Bmatrix} I & N & F \\ N' & I' & 2 \end{Bmatrix} \begin{Bmatrix} I_1 & I & I_1 \\ I' & I_1 & 2 \end{Bmatrix}. \end{aligned} \quad (\text{A4})$$

The matrix elements for the spin-rotation interaction (H_{IN}) are given by

$$\begin{aligned} \langle NM_N(I_1 I_1) IM_I | H_{\text{IN}} | N' M_{N'}(I_1 I_1) I' M_{I'} \rangle \\ = \delta_{NN'} \delta_{II'} c_1 (-1)^{N-M_N-M_{I'}+2I_1+1} 2(2I+1) \\ \times \{(2N+1)N(N+1)(2I_1+1)I_1(I_1+1)\}^{1/2} \begin{Bmatrix} I_1 & I & I_1 \\ I & I_1 & 1 \end{Bmatrix} \\ \times \sum_p \left[(-1)^p \begin{pmatrix} N & 1 & N \\ -M_N & p & M_{N'} \end{pmatrix} \begin{pmatrix} I & 1 & I \\ -M_I & -p & M_{I'} \end{pmatrix} \right], \end{aligned} \quad (\text{A5})$$

$$\begin{aligned} \langle N(I_1 I_1) IFM_F | H_{\text{IN}} | N'(I_1 I_1) I' F' M_{F'} \rangle \\ = -2 \delta_{NN'} \delta_{II'} \delta_{FF'} \delta_{M_F M_{F'}} c_1 (-1)^{F+2I_1-M_F-I} \\ \times (2F+1)(2I+1) \{(2N+1)N(N+1)(2I_1+1)I_1 \\ \times (I_1+1)\}^{1/2} \begin{Bmatrix} I_1 & I & I_1 \\ I & I_1 & 1 \end{Bmatrix} \\ \times \sum_{F'', M_{F''}} \left[(-1)^{F''+M_{F''}} (2F''+1) \begin{Bmatrix} N & F & I \\ F'' & N & 1 \end{Bmatrix} \right. \\ \left. \times \sum_p \left[(-1)^p \begin{pmatrix} F & 1 & F'' \\ -M_F & p & M_{F''} \end{pmatrix} \begin{Bmatrix} I & F'' & N \\ F & I & 1 \end{Bmatrix} \right] \right]. \end{aligned} \quad (\text{A6})$$

The matrix elements for the scalar nuclear spin-spin interaction (H_{sc}) are given by

$$\begin{aligned} \langle NM_N(I_1 I_1) IM_I | H_{\text{sc}} | N' M_{N'}(I_1 I_1) I' M_{I'} \rangle \\ = \delta_{NN'} \delta_{M_N M_{N'}} \delta_{II'} \delta_{M_I M_{I'}} \frac{1}{2} c_4 [I(I+1) - 2I_1(I_1+1)], \end{aligned} \quad (\text{A7})$$

$$\begin{aligned} \langle N(I_1 I_1) IFM_F | H_{\text{sc}} | N'(I_1 I_1) I' F' M_{F'} \rangle \\ = \delta_{NN'} \delta_{II'} \delta_{FF'} \delta_{M_F M_{F'}} \frac{1}{2} c_4 [I(I+1) - 2I_1(I_1+1)]. \end{aligned} \quad (\text{A8})$$

The matrix elements for the tensor nuclear spin-spin interaction (H_t) are given by

$$\begin{aligned} \langle NM_N(I_1 I_1) IM_I | H_t | N' M_{N'}(I_1 I_1) I' M_{I'} \rangle \\ = -c_3 \sqrt{30} (-1)^{I-M_I-M_{N'}} I_1(I_1+1)(2I_1+1) \\ \times \{(2N+1)(2N'+1)\}^{1/2} \{(2I+1) \end{aligned}$$

$$\times (2I' + 1) \}^{1/2} \begin{pmatrix} N & 2 & N' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} I_1 & I_1 & 1 \\ I_1 & I_1 & 1 \\ I & I' & 2 \end{Bmatrix} \\ \times \sum_p \left[(-1)^p \begin{pmatrix} N & 2 & N' \\ -M_N & p & M_{N'} \end{pmatrix} \begin{pmatrix} I & 2 & I' \\ -M_I & -p & M_{I'} \end{pmatrix} \right], \quad (\text{A9})$$

$$\langle N(I_1 I_1) IFM_F | H_{IZ} | N'(I_1 I_1) I' F' M_{F'} \rangle \\ = -\delta_{FF'} \delta_{M_F M_{F'}} c_3 \sqrt{30} (-1)^{N'+N+I+F} I_1 (I_1 + 1) (2I_1 + 1) \\ \times \{ (2N + 1)(2N' + 1)(2I + 1)(2I' + 1) \}^{1/2} \begin{pmatrix} N & 2 & N' \\ 0 & 0 & 0 \end{pmatrix} \\ \times \begin{Bmatrix} N & I & F \\ I' & N' & 2 \end{Bmatrix} \begin{Bmatrix} I_1 & I_1 & 1 \\ I_1 & I_1 & 1 \\ I & I' & 2 \end{Bmatrix}. \quad (\text{A10})$$

The matrix elements for the nuclear Zeeman term (H_{IZ}) are given by

$$\langle NM_N(I_1 I_1) IM_I | H_{IZ} | N' M_{N'}(I_1 I_1) I' M_{I'} \rangle \\ = -\delta_{NN'} \delta_{M_N M_{N'}} \delta_{II'} \delta_{M_I M_{I'}} g_I \mu_N B_Z (1 - \sigma_1) M_I, \quad (\text{A11})$$

$$\langle N(I_1 I_1) IFM_F | H_{IZ} | N'(I_1 I_1) I' F' M_{F'} \rangle \\ = -\delta_{NN'} \delta_{II'} \delta_{M_F M_{F'}} g_I \mu_N B_Z (1 - \sigma_1) (-1)^{2F-M_F} (-1)^{N+2I_1} \\ \times (2I + 1) \{ 4(2F' + 1)(2F + 1)(2I_1 + 1) I_1 (I_1 + 1) \}^{1/2} \\ \times \begin{pmatrix} F & 1 & F' \\ -M_F & 0 & M_{F'} \end{pmatrix} \begin{Bmatrix} I & F & N \\ F' & I & 1 \end{Bmatrix} \begin{Bmatrix} I_1 & I & I_1 \\ I & I_1 & 1 \end{Bmatrix}. \quad (\text{A12})$$

The matrix elements for the rotational Zeeman effect (H_{NZ}) are given by

$$\langle NM_N(I_1 I_1) IM_I | H_{NZ} | N' M_{N'}(I_1 I_1) I' M_{I'} \rangle \\ = -\delta_{NN'} \delta_{M_N M_{N'}} \delta_{II'} \delta_{M_I M_{I'}} g_I \mu_N B_Z M_N, \quad (\text{A13})$$

$$\langle N(I_1 I_1) IFM_F | H_{NZ} | N'(I_1 I_1) I' F' M_{F'} \rangle \\ = -\delta_{NN'} \delta_{II'} \delta_{M_F M_{F'}} g_I \mu_N B_Z (-1)^{N+I+F+F'-M_F+1} \\ \times \{ (2F' + 1)(2F + 1)(2N + 1)N(N + 1) \}^{1/2} \\ \times \begin{pmatrix} F & 1 & F' \\ -M_F & 0 & M_{F'} \end{pmatrix} \begin{Bmatrix} N & F & I \\ F' & N & 1 \end{Bmatrix}. \quad (\text{A14})$$

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